



Application No. 10/ 714,083

Attorney Docket No: QUT-102

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Ari Aviram

Application No.: 10/714,083  
2823

Group Art Unit:

Filed: November 15, 2003  
Coleman

Examiner: William D.

Title: ELECTRICAL CONTACTS FOR MOLECULAR ELECTRONIC  
TRANSISTORS

AFFIDAVIT UNDER 37 C.F.R. ' 1.131 OF  
ARI AVIRAM, Ph.D.

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Ari Aviram, hereby declare and state that:

1. I am the sole inventor of the subject matter disclosed and claimed in the above-referenced patent application. I am familiar with the Office Action mailed April 11, 2005.

2. I have been informed by patent counsel that Claims 1-15 of the above-referenced patent application have been rejected by the U.S. Patent and Trademark Office under 35 U.S.C. § 102(e) as being anticipated by Tanabe *et al.*, U.S. Patent Application Publication No. 2004/ 0012018 A1 published January 22, 2004, for US Appl. No.

10/619,566 filed July 16, 2003 and claiming priority to JP Appl. 2002-208212 filed July 17, 2002.

3. The invention described and claimed in the above-referenced patent application, U.S. 10/714,083, was completed in the United States before July 16, 2003. The documented work was performed at Qutronics, Inc., 444 Bramblebush Road, Croton on Hudson, NY 10520, and at 1725 Front St., Yorktown Heights, NY 10598.

4. The invention described and claimed in U.S. 10/714,083 was conceived and reduced to practice prior to July 16, 2003, the effective date under 35 U.S.C. § 102(e) of the Tanabe *et al* reference cited by the Examiner.

5. In order to establish reduction to practice prior to July 16, 2003, and conception of the invention prior to said date coupled with due diligence from prior to said date to the filing of the application on November 15, 2003, attached hereto are the following Exhibits (Exhibit A through Exhibit D) that support the swearing back of the reference under 37 C.F.R. § 1.131. An explanation of each of the Exhibits, pointing out exactly what facts are established and relied on by Applicant follows the description of each Exhibit:

“**Exhibit A**” is a photocopy of the original document, “Single Company Advanced Technology Program (ATP) Proposal”, hereinafter, the “ATP Proposal” submitted by me to the U.S. Department of Commerce ATP Program on September 27, 2002. Of particular relevance are pages 8-20, wherein is described in detail the plan for design and synthesis of molecular electronic

transistors according to the invention described and claimed in U.S. 10/714,083. Much of the language of pages 8-20 was incorporated into my Specification.

Exhibit A describes the elements of my amended Claim 1 as follows.

At page 8 of my ATP Proposal, second to last paragraph, last sentence, it is stated that "Figure 2 shows a possible implementation of such a molecular device." The last paragraph of page 8 describes a mechanism of operation of a planar molecular electronic transistor according to my invention. Figure 2 on page 9 of the ATP proposal is similar to Figure 4 of my patent application, and shows wiring a three-terminal molecule comprising a source terminal, a gate terminal, and a drain terminal to serve as a molecular electronic transistor, the electronic transistor comprising the molecule attached to a gate electrode, a source electrode, and a drain electrode, wherein the source electrode and the drain electrode are fabricated from a metal that can attach to a thiol (-SH) group, and the gate electrode is fabricated from a metal that can attach to a different moiety (X). It is clear from Figure 2 of the ATP Proposal that the source and the drain terminals could attach to the same or different metal, such as, e.g., platinum or gold, which are known to bond to -SH groups, and that the gate terminal has a different moiety, X, which can attach to the gate electrode.

At least on page 15 of the ATP proposal is further support for my Claim 1 limitation which provides that the source electrode and the drain electrode are fabricated from a first previously-determined metal and the gate electrode is fabricated from a second previously-determined metal.

For example, in the first four lines of the last paragraph on page 15 it is stated that:

The circuit will be made of platinum for the source and the drain connections, and of aluminum for the gate connection. The molecules will contain -SH groups on the source and drain terminals and phosphates on the gate terminal. (p.15, last paragraph.)

Also on page 15 of my ATP proposal is an example of support for my Claim 1 limitation of functioning to allow for simultaneous attachment of the molecule to the source electrode, drain electrode, and gate electrode in a previously-determined order. For example, in paragraph 2 on page 15 it is stated that:

By distinguishing between the gate-electrode metal and the metal used for the source and drain electrodes, an opportunity arises to direct the three terminals of the molecule to the proper arrangement. This can be accomplished by providing the molecule with specific alligator clips for binding the source/drain ends of the molecule to source/drain electrodes, and a specific alligator clip for binding the gate end of the molecule to the gate electrode. For example, the gate electrode can be made of aluminum, which will couple specifically to a phosphate alligator clip on the molecule, (gate chain) and the source/drain electrodes can be made of gold or platinum, which will couple specifically to -SH alligator clips on the corresponding chain. These considerations guide the design of the molecules (task 1) and the design of the metal-electrode patterns (task 2). (page 15, paragraph 2.)

Also on page 15 of the ATP proposal is an example of support for my Claim 1 limitation of allowing the molecule to attach to the source electrode, the drain electrode, and

the gate electrode in the previously-determined order, thereby forming the nanometer-scale circuit. For example, in paragraph 4, lines 4-6, on page 15 it is stated that:

The molecules will be attached to the three terminals by self-assembly, either as neutral species or as doubly charged species.

(Paragraph 4, page 15.)

Another example of support for the limitation can be found on page 19 under "Task 4- Self -assembly", paragraph 2, wherein it is stated that: "To accomplish the self-assembly process, the patterned surfaces are dipped into a solution that contains the molecules."

See also, page 11 of the ATP proposal, second to last paragraph, wherein it is stated: "2. The molecular transistors are added to the metallized (prepared) surfaces by self-assembly, bridging the open gaps of the metal pattern." See also, page 16, "Task 1- Synthesis of molecular transistors."

Support for the preamble of Claim 1, "A method of forming at least one nanometer-scale circuit comprising a molecular electronic transistor and electrical contacts therefore, ..." is evident throughout the ATP proposal, e.g., on page 18 under "Task 3- Thin-film patterning", lines 4-5, wherein it is stated that "Gaps provided by the lithographic process will match the length of the transistor molecule which will have to bridge those gaps." See also, the last two lines of page 18: "Nanometer-size metal patterns are fabricated in several steps..."

See also "**Exhibit B**", a photocopy of the original letter, dated October 17, 2002, from the Competitions

Manager of the Advanced Technology Program, acknowledging receipt of the above-described proposal. Applicant relies on the date of the referenced letter as evidence of conception of the claimed invention prior to July 16, 2003.

6. I worked diligently from prior to May 6, 2003 to prepare and file a regular U.S. patent application. As one of the initial steps I took to prepare the claims for my patent application, I authorized and paid for a Patent Prior Art Search, the search conducted by the Intellectual Resources Group. (See **"Exhibit C"**, copy of cancelled check dated May 6, 2003 in payment for the search.) Applicant relies in part on the date of the cancelled check for the prior art search as evidence of due diligence from prior to July 16, 2003 to the filing of the application on November 15, 2003.

7. **"Exhibit D"** is a short summary of my relevant education and experience. I believe that the facts stated in the summary show that I have significant knowledge and experience in the field of molecular electronics, as well as familiarity with related scientific literature. I am not aware of the existence of any technology or devices that are similar to the invention claimed in my patent application. Tanabe's application is for an organic semiconductor device. Properties of semiconductor materials, whether organic or silicon-based, are properties of bulk materials, and cannot be observed in single molecules. My patent application is directed towards a molecular electronic device in which a single molecule is wired as a transistor; and to the best of my knowledge, this has not been accomplished prior to my

invention.

8. The attached Exhibits (**Exhibit A through Exhibit B**) establish that, prior to July 16, 2003, I, as the Applicant of the above-referenced patent application conceived and reduced to practice the invention claimed in Claims 1 through 15. Attached **Exhibit C**, copy of cancelled check dated May 6, 2003 in payment for the patent prior art search, is evidence of due diligence from prior to July 16, 2003 to the filing of the application on November 15, 2003.

9. I further state that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false statements, and the like so made, are punishable by fine or imprisonment, or both under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

**Attachment: Exhibits A-D**

Executed this August 9, 08 day of August, 2005.

Ari Aviram

Ari Aviram

State/Commonwealth: New York

County  
of

Dutchess

Then personally appeared before me the above-named **Ari Aviram** and acknowledged that he executed the foregoing instrument as his free act and deed this 9<sup>th</sup> day of August, 2005.

(SEAL)

**JEFFREY A. ECONOM**  
Notary Public, State of New York  
No. 4953159  
Qualified in Dutchess County  
Term Expires July 8, 20 07

Jeffrey A. Econom

Notary Public

JEFFREY A. Econom

(print name)

My Commission expires 07 / 03 / 07



ST-1202  
TV-7-2000)  
O-203-26U.S. DEPARTMENT OF COMMERCE  
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGYSINGLE COMPANY ADVANCED TECHNOLOGY PROGRAM  
(ATP) PROPOSAL COVER SHEET  
(CATALOG OF FEDERAL DOMESTIC ASSISTANCE NUMBER 11.612)

2002

Public reporting burden for this collection of information is estimated to average thirty (30) hours per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Director, Advanced Technology Program, National Institute of Standards and Technology, 100 Bureau Drive, Stop 4700, Administration Building, Room A333, Gaithersburg, Maryland 20899-4700.

1. COMPETITION NUMBER 2002	2. TECHNOLOGY AREA CODE E9900	3. PROJECT DURATION 3 YEARS MONTHS
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4A. OTHER ATP SUBMISSIONS LIST PROPOSAL NUMBER(S) OF SUBSTANTIALLY OVERLAPPING PROPOSAL(S) PREVIOUSLY SUBMITTED 2002-00-4931	4B. IF SUBMITTING A CONCURRENT SUBSTANTIALLY OVERLAPPING PROPOSAL TO ANOTHER CURRENT OR PENDING ATP COMPETITION, LIST COMPETITION NUMBER(S)
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5. LEGAL NAME, ADDRESS, AND WEBSITE OF SUBMITTING ORGANIZATION  Qutronics Inc. 444 Bramblebush Rd. Croton On Hudson, NY 10520	6. TYPE OF ORGANIZATION (CHECK ALL THAT APPLY)  <input checked="" type="checkbox"/> PROFIT - SMALL BUSINESS <input type="checkbox"/> PROFIT - LARGE BUSINESS <input type="checkbox"/> PROFIT - MEDIUM BUSINESS <input type="checkbox"/> FOREIGN-OWNED U.S. SUBSIDIARY
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7. EMPLOYER IDENTIFICATION NUMBER (EIN) 13-4193304	8. DUN AND BRADSTREET NUMBER 051685787
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9. NAME OF PRINCIPAL INVESTIGATOR AT SUBMITTING ORGANIZATION (Address required, if different than Item 5)	10. NAME OF GRANT/CONTRACT MANAGER AT SUBMITTING ORGANIZATION (Address required, if different than Item 5)
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TELEPHONE NUMBER: (914) 414 8639, (914) 245 8200  
FAX NUMBER:  
E-MAIL ADDRESS: aviram@qutronics.com

TELEPHONE NUMBER:  
FAX NUMBER:  
E-MAIL ADDRESS:

11. SOURCES OF FUNDS	YEAR ONE	YEAR TWO	YEAR THREE	TOTAL
A. ATP (DIRECT COSTS ONLY)	\$ 712,133.30	\$ 653,933.30	\$ 633,933.30	\$2,000,000
B. PROPOSER	\$ 50,000	\$ 50,000	\$ 50,000	\$150,000
C. TOTAL (A + B)	\$ 762,133.30	\$ 703,933.30	\$ 683,933.30	\$2,150,000

12. PROPOSAL TITLE Molecular integrated circuits
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## 13. NON-PROPRIETARY PROPOSAL ABSTRACT

The objective of this proposal is to demonstrate the feasibility of producing molecular transistors and integrating them into high-density memory SRAM and DRAM devices that exceed the storage capacity of current commercial memory chips based on CMOS technology. The individual memory elements measure up to 10nm x 10 nm and thus are candidates for very large memory chips of terabit size. The proposal is based on theoretical and experimental results published in the open literature. The intent is to place the transistor molecules in gaps between metal electrodes, that are a few nanometer apart. The metal electrodes are part of the integrated circuit. The advantages of molecular electronic technology are: a) high density, b) low power and c) low cost.

10/714,083  
Exhibit A

STATEMENT: BY SIGNING THIS PROPOSAL COVER SHEET, I CERTIFY, TO THE BEST OF MY KNOWLEDGE AND BELIEF, THAT ALL INFORMATION IN THIS PROPOSAL IS TRUE AND CORRECT AND THAT:

THE PROPOSAL IS NOT REQUESTING FUNDING FOR EXISTING OR PLANNED RESEARCH PROGRAMS THAT WOULD BE CONDUCTED IN THE SAME TIME PERIOD IN THE ABSENCE OF FINANCIAL ASSISTANCE UNDER THE ATP.

THE INDIRECT COSTS PROPOSED IN THIS PROPOSAL ARE INCLUDED UNDER THE PROPOSER'S COST SHARE AND NO INDIRECT COSTS ARE INCLUDED IN THE ATP SHARE OF COSTS REQUESTED.

IF THE LARGE BUSINESS, COST SHARING PROPOSED BY THE LARGE BUSINESS IS AT LEAST 60 PERCENT OF EACH YEAR'S TOTAL COSTS.

THE TOTAL VALUE OF ANY IN-KIND CONTRIBUTIONS DOES NOT EXCEED 30 PERCENT OF THE COMPANY'S TOTAL COST SHARE.

THE FOLLOWING QUESTIONS HAVE BEEN TRUTHFULLY ANSWERED:

	YES	NO
IS THE COMPANY DELINQUENT ON ANY FEDERAL DEBT? (IF YES, EXPLAIN IN ITEM 15, REMARKS.)	<input type="checkbox"/>	<input checked="" type="checkbox"/>
WAS PROPOSAL OR VERY SIMILAR PROPOSAL SUBMITTED TO ANOTHER FEDERAL AGENCY? (IF YES, EXPLAIN IN ITEM 15, REMARKS.)	<input type="checkbox"/>	<input checked="" type="checkbox"/>
DOES THE COMPANY HAVE A PARENT COMPANY OUTSIDE THE UNITED STATES? (IF YES, IDENTIFY THE PARENT COMPANY AND ITS PLACE OF INCORPORATION IN ITEM 15, REMARKS.)	<input type="checkbox"/>	<input checked="" type="checkbox"/>
IS THE COMPANY MAJORITY OWNED BY INDIVIDUALS WHO ARE NOT CITIZENS OF THE UNITED STATES? (IF YES, EXPLAIN IN ITEM 15, REMARKS.)	<input type="checkbox"/>	<input checked="" type="checkbox"/>
IS THE COMPANY SUBJECT TO CONTROL BY INDIVIDUALS WHO ARE NOT CITIZENS OF THE UNITED STATES? (IF YES, EXPLAIN IN ITEM 15, REMARKS.)	<input type="checkbox"/>	<input checked="" type="checkbox"/>
DOES THE PROPOSED R&D INVOLVE THE USE OF HUMAN SUBJECTS AND/OR HUMAN TISSUE, AND/OR HUMAN CELL LINES? (IF YES, EXPLAIN IN ITEM 15, REMARKS, AND INDICATE WHETHER OR NOT THE RESEARCH PLAN HAS BEEN REVIEWED AND APPROVED BY AN INSTITUTIONAL REVIEW BOARD (IRB).)	<input type="checkbox"/>	<input checked="" type="checkbox"/>
DOES THE PROPOSED R&D INVOLVE THE USE OF VERTEBRATE ANIMALS? (IF YES, EXPLAIN IN ITEM 15, REMARKS, AND INDICATE WHETHER OR NOT THE RESEARCH PLAN HAS BEEN REVIEWED AND APPROVED BY AN ANIMAL CARE AND USE COMMITTEE.)	<input type="checkbox"/>	<input checked="" type="checkbox"/>

REMARKS (CONTINUE ON A SEPARATE SHEET IF NECESSARY)

DESCRIBE WHAT EFFORTS WERE MADE, PRIOR TO APPLYING FOR ATP FUNDING, TO SECURE PRIVATE CAPITAL TO SUPPORT THIS PROJECT WHOLLY.

We attempted to receive venture capital for this project from several companies. The following three companies did discuss with us possible investment: DFJ of Santa Clara California, DFJG of New York, NY, and Oxford Biosciences Partners from Boston, MA. All three companies expressed an opinion that it is too early for them to invest at this stage.

AUTHORIZED COMPANY REPRESENTATIVE (TYPE NAME AND TITLE)

Ari Aviram

18. TELEPHONE NUMBER

(914) 414 8639

SIGNATURE

*Ari Aviram*

20. DATE

09/27/2002

## ESTIMATED MULTI-YEAR BUDGET - SINGLE COMPANY

	YEAR ONE	YEAR TWO	YEAR THREE	TOTAL
<b>OBJECT CLASS CATEGORY</b>				
Personnel Salaries/Wages	\$ 430,000	\$ 370,000	\$ 370,000	\$ 1,170,000
Personnel Fringe Benefits	80,000	51,800	51,800	183,600
Travel	15,000	15,000	15,000	45,000
Equipment	40,000	30,000	10,000	80,000
Materials/Supplies	50,000	50,000	50,000	150,000
Contracts	80,000	120,000	120,000	320,000
Other	17,133.30	17,133.30	17,133.30	51,400
<b>Total Direct Costs (Lines A thru G)</b>	<b>712,133.30</b>	<b>653,933.30</b>	<b>633,933.30</b>	<b>2,000,000</b>
<b>Total Direct Costs Requested From ATP</b>	<b>712,133.30</b>	<b>653,933.30</b>	<b>633,933.30</b>	<b>2,000,000</b>
<b>Total Direct Costs Shared by Proposer (If Any)</b>	<b>\$</b>	<b>\$</b>	<b>\$</b>	<b>\$</b>
<b>Total Indirect Costs Absorbed by Proposer</b>	<b>\$ 50,000</b>	<b>\$ 50,000</b>	<b>\$ 50,000</b>	<b>\$ 150,000</b>
<b>Total Costs (Lines H + K)</b>	<b>\$ 762,133.30</b>	<b>\$ 703,933.30</b>	<b>\$ 683,933.30</b>	<b>\$ 2,150,000</b>
<b>SOURCES OF FUNDS</b>				
ATP (Same as Line I)	\$ 712,133.30	\$ 653,933.30	\$ 633,933.30	\$ 2,000,000
Qutronics Inc.	50,000	50,000	50,000	150,000
<b>Total Sources of Funds (Same as Line L)</b>	<b>\$ 762,133.30</b>	<b>\$ 703,933.30</b>	<b>\$ 683,933.30</b>	<b>\$ 2,150,000</b>
<b>TASKS</b>				
	\$	\$	\$	\$
<b>Total Costs of All Tasks (Same as Line L)</b>	<b>\$</b>	<b>\$</b>	<b>\$</b>	<b>\$</b>

## SUBCONTRACTS

NAME AND ADDRESS OF SUBCONTRACTOR

## 2. TYPE OF ORGANIZATION (CHECK ALL THAT APPLY)

- |   |  |
|---|--|
| <input type="checkbox"/> PROFIT - SMALL BUSINESS                      | <input type="checkbox"/> PROFIT - LARGE BUSINESS       |
| <input type="checkbox"/> PROFIT - MEDIUM BUSINESS                     | <input type="checkbox"/> FOREIGN-OWNED U.S. SUBSIDIARY |
| <input type="checkbox"/> NON-PROFIT INDEPENDENT RESEARCH ORGANIZATION |  |
| <input type="checkbox"/> UNIVERSITY                                   | <input type="checkbox"/> GOVERNMENTAL LABORATORY       |

## 3. ESTIMATED AMOUNT OF SUBCONTRACT

NAME OF CONTACT:

PHONE NUMBER:

FAX NUMBER:

E-MAIL ADDRESS:

DESCRIBE SCOPE OF WORK

IS THIS A SOLE SOURCE CONTRACT?

☒ YES (IF YES, EXPLAIN) ☐ NO

NAME AND ADDRESS OF SUBCONTRACTOR

## 2. TYPE OF ORGANIZATION (CHECK ALL THAT APPLY)

- |   |  |
|---|--|
| <input type="checkbox"/> PROFIT - SMALL BUSINESS                      | <input type="checkbox"/> PROFIT - LARGE BUSINESS       |
| <input type="checkbox"/> PROFIT - MEDIUM BUSINESS                     | <input type="checkbox"/> FOREIGN-OWNED U.S. SUBSIDIARY |
| <input type="checkbox"/> NON-PROFIT INDEPENDENT RESEARCH ORGANIZATION |  |
| <input type="checkbox"/> UNIVERSITY                                   | <input type="checkbox"/> GOVERNMENTAL LABORATORY       |

## 3. ESTIMATED AMOUNT OF SUBCONTRACT

NAME OF CONTACT:

PHONE NUMBER:

FAX NUMBER:

E-MAIL ADDRESS:

DESCRIBE SCOPE OF WORK

IS THIS A SOLE SOURCE CONTRACT?

☐ YES (IF YES, EXPLAIN) ☐ NO

## Executive Summary

### Company information

Name: Qutronics Inc.,  
Address: 444 Bramblebush Rd.,  
Croton on Hudson, NY 10520  
Telephone: (914) 414 8639  
Laboratory address:  
1725 Front Street,  
Yorktown Heights, NY 10598  
Email: [aviram@qutronics.net](mailto:aviram@qutronics.net)

### Research title

#### Molecular integrated circuits

### Technical rationale

Molecular Electronics is an emerging technology that is being vigorously pursued by research institutions and large commercial companies around the globe. The field has been defined by several theoretical and experimental publications which describe and demonstrate electronic properties of molecules. These properties are directly applicable to the microelectronics industry. Among these are a series of recent publications from Yale and Rice universities describing an experimental demonstration of a molecular negative-differential-resistance switch. Earlier theoretical work describes field-effect transistors based on switches created by double-well molecular properties. Electric fields can turn on and off the electrical conductivity of these switches, a process synonymous with switching a transistor by the application of a gate voltage. It is conceivable that such molecules can be used to replace conventional transistors in circuits of logic and memory.

The interconnection of molecules to form integrated circuits is a "bottom-up" process whereby the molecules are attached to prefabricated arrays of electrodes. The metal lines that are used for the wiring of the circuit contain, in locations designated for transistors, gaps that are precisely sized to accommodate the molecules. The attachment takes place in one step by a technique called "self-assembly." This technique was developed in surface science for the specific attachment of molecules to surfaces in single layers.

Molecular integrated circuits can be manufactured by means of the following steps:

1. Molecular transistors are synthesized by conventional chemistry techniques.
2. Designated surfaces are covered with multi-electrode nanojunctions. The electrodes are fabricated by lithographic techniques in the circuit pattern.
3. Transistor molecules are inserted in the nanojunctions by self-assembly techniques.

This nanofabrication process is much simpler than the multi-step processes for fabricating conventional integrated circuits, and can lead to substantial savings in manufacturing. Other attributes of molecular devices are high density, low power density, and high speed.

### **Proposed innovations**

Despite the high level of activity in the field of molecular electronics and the successful demonstration of molecular field-effect transistors, there is still a need for additional innovation in order to realize actual implementation of molecular technology. This work will pursue the reduction to practice of a transistor based on double-well potential molecules. Such transistors can have latching or nonlatching properties, and may be suitable for ultra-dense SRAM memories. In addition, the project will pursue the attachment and characterization of the molecular transistors in small circuits and will demonstrate SRAM memory circuits. The proposed new transistors will be planar, a structural property that will make their attachments relatively simple. Though there is a clear concept of the technology, several scientific results must be put into practice.

### **Technical risks**

The theoretical foundations of this project are solid, and a large number of experimental pieces have been demonstrated. Still, many details of the technology have not been worked out, and considerable work remains to be done. There has not yet been an experimental demonstration of a molecular integrated circuit, and the details of integration may prove to require several new inventions.

### **Potential for broad-based economic benefits**

The introduction of a molecular technology into the marketplace will have a profound effect on the data processing industry because of the new applications that it will offer. The high density of molecular devices that can be packed into one microchip could be used to create ultra-dense memories that will hold the content of hundreds of books or manuals. These molecular devices could be used in supercomputers to solve problems that are beyond the capability of current supercomputers. This new technology has the capability to stimulate the growth of the world economy to unprecedented levels.

In the year 2000 the market for semiconductor components has reached \$200 billion, and it is expected to double in size in the next five years. Molecular technology will capture a portion of this market and will grow in subsequent years.

### **Need for ATP funding**

Molecular electronics as a technology is still in its infancy. Few venture capital companies are willing to fund projects at such an early stage, and our efforts to obtain private financing for the project have met with resistance. ATP could

pave the way to secure commercial investment and lead to commercial implementation through alliances with large corporations.

### **Pathways to economic benefits**

Our company will develop the basic technology for production of molecular integrated circuits. It will also develop commercial prototypes of electronic components, such as SRAM. The presence of working prototypes will help foster commercial relationships with large companies who will be interested to participate in the technology and turn it into a commercial success.

## **Scientific and Technological Merit**

### **Introduction**

The tidal wave of technological innovation that is currently sweeping the world in biology, medicine, pharmacology, and electronics can be traced to a tiny electronic component known as the transistor. Of all the devices known to man, the transistor has made possible more new products and improved more existing products than any other device. Since the invention of the transistor and its incorporation into integrated circuits (IC) by Noyce and Kilby in 1959, increasing numbers of transistors have been packaged together to form devices such as memories, microprocessors, and large logic modules. Today's microcircuit technology brings to market chips with the dimensions of a pinhead that contain one-gigabit memories. This astonishing success can be attributed to the industry's reliance on the process of scaling known as Moore's law (1), which predicts exponential growth of integrated-circuit complexity. While the fortunes of the semiconductor industry have also experienced exponential growth in parallel with the process of miniaturization, Moore's law, to the distress of many, is about to reach its limit. It is apparent that the trend of miniaturization in silicon devices is about to lose momentum, and this time the foreseen barriers are fundamental, with no currently known solutions (2).

The technological difficulties facing the semiconductor industry are real. They have led to extensive research (3) because of the perception that the growth of the industry will slow dramatically if no timely solution is found. The difficulties are related to the low number of switching electrons in future transistor gates, and to the projected undesirable electron leaks in future transistor gate oxide. The gate oxide, which in current transistors is 25 angstroms thick, is projected by the Semiconductor Industry Association (SIA) to shrink to 10 angstroms in devices that are planned for the year 2012 (4). Both experiment and theory show that pinhole-free 10-angstrom silicon-oxide gates cannot be reliably fabricated. Thus, the search continues for new gate materials and for other innovations that will alleviate the predicted problems. A recent issue of the *IBM Journal of Research and Development* called "Scaling CMOS to the Limit" (3) is devoted to these problems and their solutions.



Another unacceptable roadblock in conventional silicon technology is the projected high cost of fabrication. It is expected that the cost of a semiconductor factory (fab) will rise to about \$50 billion by the year 2012 (2). A significant reduction of the cost of fabrication is an important challenge facing the industry, and adding complexity to the device will only exacerbate this problem. This challenge can be met only through a radical change of the fabrication process.

The difficulties foreseen by the semiconductor industry are so great that they have been termed "the red brick wall" (2). However, despite the gloomy predictions, the industry is optimistic about the prospects for the future (3). Nevertheless, it is exploring all possibilities by developing alternative approaches to scaling of CMOS technology. These approaches are known in the industry as "nanotechnology." Molecular Electronics (ME) is a branch of nanotechnology.

### Recent advances in molecular electronics

A recent Bell Laboratories report in *Nature* by Schon et al. describes new monolayer field-effect transistors (FETs) and inverters (5). The report represents an important step toward molecular-scale electronics\*. The report demonstrates that the transistor has gain (the ratio of the out-current to the gate in-current) of approximately six orders of magnitude.

The device described in this report was made by forming the gate on a highly doped Si substrate which was patterned with conventional lithography and anisotropic etching in order to define a step. 30 nm of thermally grown oxide was deposited on the riser of the step to serve as the gate insulator. Molecules were deposited vertically along the wall of the step by attaching them to a gold electrode that was placed at the bottom of the step. This electrode defined the source of the transistor. A second gold electrode (the drain) was deposited on the top edge of the step with the molecules in place.

The current-voltage characteristics of the molecule 4,4'-biphenyldithiol are similar to those of CMOS transistors. The data indicates that the device is in fact a normally off p-channel transistor with threshold voltage of approximately -0.2 volts. The authors did not report on the capacitance ( $C$ ) of this transistor; however, it can easily be estimated from the dimensions of the device. Calculation of the current modulation capability of the device by calculating  $CV/I$  leads to the conclusion that this device is almost as fast as a single-crystal Si CMOS transistor.

Another molecular device that has recently received considerable attention is based on negative differential resistance (NDR) and is being considered for large scale DRAM (6).

In a recent publication, Ellenbogen and Love have shown how NDR components and rectifier components can be used as building blocks of large memory cells and logic devices (7).

The work cited here represents significant progress in the field of molecular electronics.

\* The reader should note that *The New York Times* reported on May 21 and May 23, 2002 that a dispute exists regarding the results published in reference 5.



## Theoretical background for this proposal - Intervalence electron transfer

Long-distance intervalence electron transfer occurs in mixed-valence compounds. On the molecular scale, these compounds contain two or more redox sites of different oxidation states (the term "redox" is derived from the words reduced - oxidized). Each of the redox sites contains different organic or organometallic moieties that can exist in several oxidation states, in the general form of M-spacer-M<sup>+</sup>. Such materials belong to a general class of compounds known as the Creutz-Taube family, also known as flexomers (8).

The potential energy curves of mixed-valence compounds as a function of electron transfer coordinates are obtained from the zero-order structure, defined when two non-interacting states (the end groups) Red-Ox and Ox-Red are considered. For such states, the potential energy vs. reaction coordinates  $Q$  is represented by two parabolas. A reorganization energy ( $\lambda$ ) is invested in the process of converting one flexomer into the other. When the two states are allowed to interact, the two separate parabolas merge into a double-well potential with an electron coupling parameter  $V_{ab}$ . Hush (9) has shown that there are two intramolecular electron-transfer mechanisms: a thermal one and an optical one. In the limit of zero electronic interaction, the thermal activation energy is 1/4 of the optical energy because of the parabolic nature of the curve. When there is electronic interaction between the two conformers, the system can jump from one zero-order parabola to the other, passing through the "forbidden crossing" region (the intersection between the two parabolas) with a thermal electron transfer rate that is proportional to  $(V_{ab})^2$ . Thus,  $V_{ab}$  is an important parameter that can be determined from

spectroscopic data by Hush's equation:

$$V_{ab} = \frac{2.05 \cdot 10^{-2} \sqrt{\nu \Delta \nu \epsilon_{\max}}}{R_{MM}}$$

Here  $\epsilon_{\max}$  is the maximum extinction coefficient for the intervalence transition,  $\nu$  is the energy ( $\text{cm}^{-1}$ ),  $\Delta \nu$  is its full width at half maximum, and  $R_{MM}$  is the distance between the redox sites.

According to quantum mechanics, an electric field  $F$  will tilt the two minima of a double-well potential belonging to Red-Ox - spacer - Ox-Red flexomer by an amount of energy proportional to the dipole moment ( $\mu$ ) of the molecule. This induced tilt of the minima (called the "chemical potential" or "exothermicity") can promote a transition of an electron from the Red-Ox site to the Ox-Red site. Such a transition amounts to the switching of one conformer to the other. The magnitude of the electric-field-induced chemical potential is equal to  $2 \mu F$ . As the magnitude of the applied electric field increases, the barrier between the two minima of the double-well potential decreases to a point at which the diabatic activation energy vanishes. The field that is needed to reach this point is called the critical field ( $F_{\text{crit}}$ ).  $F_{\text{crit}}$  can be calculated from the following equation (10):

$$F_{crit} = \frac{\lambda}{2\mu}$$

The calculated critical field for 100% switching of molecules described in this proposal is  $10^5$  V/cm (11), which is well below the range of fields applied on molecules in scanning tunneling spectroscopy without causing decomposition. At this critical field, the conversion takes place at a time characteristic of electronic conversions (namely  $10^{-15}$  seconds); however, transitions with slower rates will occur at lower applied fields, since electrons can tunnel through activation barriers.

*Later in this proposal (table 1, and the explanation given on page 9) we will present data based on experimental evidence in support of the theoretical conclusion that the rate of electron transfer in mixed-valence molecules is solely dependent on electron transfer mobility and totally independent of any counter-ion mobility, which invariably proceeds at a slower pace (8b).* Experiments have shown that the reorganization of the counter ions is accounted for in the reorganization energy term, which was found in several studies (11, 12) to be totally independent of the applied electric field.

The field of electron transfer in double-well potential molecules is well established. It has been distinguished with two Nobel prizes, which were awarded in 1983 to Henry Taube and in 1992 to Rudolph Marcus. The work of Noel Hush is also worthy of the award.

### **The proposed research**

This proposal offers a technology which can bypass the problems encountered by continuous scaling of silicon devices. The proposed new technology is based on the premise that certain molecules, such as rectifiers (13), conductors, and transistors (11, 12, 14), have properties of electronic components. Such molecules can be used as rudimentary components of circuits, and this can lead to the development of new electronic ICs of superior density and speed, which use minuscule amounts of power compared to CMOS transistors. In essence, the proposal is for the development of integrated circuits that use molecular transistors instead of conventional semiconductor transistors. An explanation of how such transistors function, and how such transistors will be incorporated into integrated circuits, is given in subsequent sections.

### **The technical principles of the proposed transistors**

The molecular transistors designated for this project are field-effect transistors. They function on the basis of several principles that have been thoroughly examined theoretically (11, 12, 14) and, in part, experimentally (15). Past experimental efforts have been focused almost entirely on the synthetic aspect of the transistor, and very important materials have been obtained. However, actual testing of the transistor's

properties has not been undertaken. The reason for this delay has been technical, arising in part from the difficulty of wiring the complicated three-dimensional molecular structure proposed in the original publication (14). An alternative approach, which makes use of a planar version of the transistor, is adopted in this proposal. This approach takes advantage of the new transistor structure to simplify its connections to the wires of the circuits. It is clearly easier to attach three metallic contacts (source, drain, and gate) to a planar molecule rather than to a three-dimensional one.

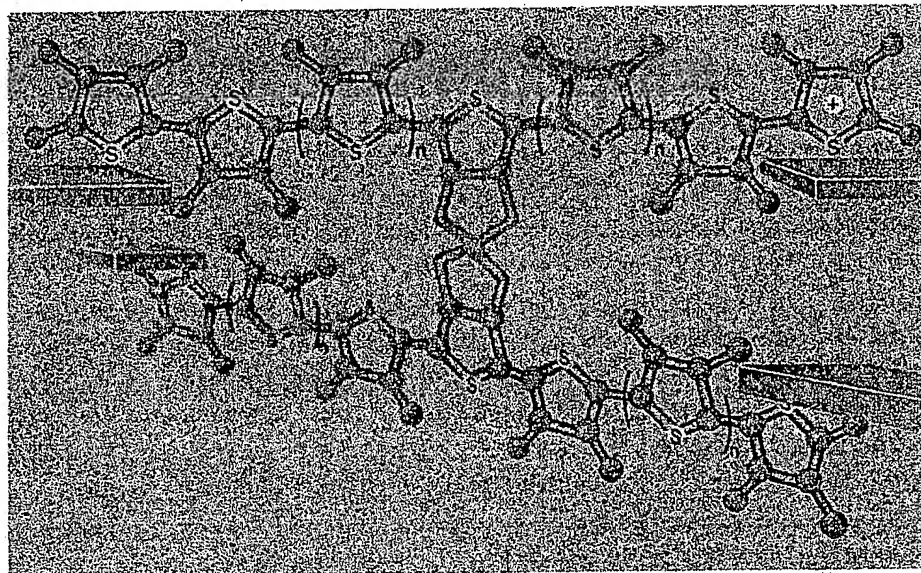


Figure 1 - A molecular field-effect transistor.

The theoretical studies carried out for the *spiro-bridge field-effect transistor* shown in Figure 1 provide the theoretical basis for the proposed investigation (14). The device can display both current switching and gain. The molecule contains two oligomeric chains that are separated by a spiro bridge whose purpose is to maintain the two chains sterically at 90 degrees to each other. This feature keeps the planes of the chains orthogonal, thus preventing electronic interaction between the chains. The bridge is also made of saturated hydrocarbons built with  $\sigma$  bonds, in contrast to the two chains, which are conjugated and contain  $\pi$  bonds. Because of its structure and bonding, the bridge is a good electronic insulator, offsetting any conjugation between the chains. Another feature of the design is that one chain is missing an electron, and overall the molecule contains an unpaired electron. At any particular time, the molecule assumes one of two different conformations (valence tautomers): one with the electrical + charge (hole) on one chain (as shown), and one with the hole on the other chain. The neutral chain contains one more electron than the charged chain. The molecule represents a double-well potential quantum-mechanical box for the "extra" electron, which, according to quantum mechanics, can tunnel from state to state, as was described in the background section on

intervalence electron transfer. It takes a mere transition (switching) of the electron to the other chain to convert the molecule from one tautomer to the other. It is a basic property of an electron in a double-well potential quantum-mechanical box to relocate from one well to the other under the influence of a properly poled electric field (10). Thus, an electric field can be used to switch among the tautomers. In the absence of an electric field, the electron will be confined to one chain or the other and, because of the orthogonal structure of the bridge, will not tunnel across spontaneously. This property has been verified experimentally by Guai et al. (16) using electron paramagnetic resonance.

Another design feature of this molecule is the high electrical conductivity of the charged (+) chain as opposed to the low conductivity (or insulation) of the neutral chain. This feature was the subject of the year-2000 Nobel Prize in chemistry awarded to Heeger, MacDiarmid, Shirakawa et al., for their discovery that insulating polymers such as polyacetylene or polyphenylene can be converted to highly conductive materials by removal of electrons from their highest occupied molecular orbitals (17). On exposure to bromine or iodine, polyacetylene is oxidized. The polymer chain loses an electron, leaving a hole of positive charge. This charge is neutralized by the bromide or iodide counter ions. The presence of a hole on the polymer chain makes possible the migration of electrons along the chain. The conductivity of polyacetylene is  $10^7$  S/m, compared to the conductivity of silver, which is  $10^8$  S/m. Thus (by analogy), the operation of the molecular field-effect transistor is as follows: One of the chains (say the neutral, nonconductive chain) is placed in an electronic circuit between a source and a drain. This chain is the transistor channel. The gate electrode is positioned perpendicularly in order to apply a field along the axis that traverses the spiro bridge. When a field with correct polarity and intensity is applied by the gate electrode, an electron is switched from the insulating chain to the other chain, switching "on" the conductivity of the device. This effect is analogous to the function of a transistor. The critical switching field is  $10^5$  V/cm, which can be generated by application of 0.1 – 0.2 V in a nanostructure.

For practical purposes, the molecular device described above is considered to be too complicated for actual testing. It requires a minimum of two electrodes in the plane of the molecule and two electrodes (not shown in Figure 1) placed perpendicular to the molecule, with at least one of them out of the plane (18). A solution to this problem was proposed (19) but never implemented; it was suggested that one of the chains of the molecule shown in Figure 1 be replaced by a different moiety that could serve as a donor / acceptor of electrons, thus preserving the essential features of the transistor but in a planar configuration. Figure 2 shows a possible implementation of such a molecular device.

In this example, one of the polythiophene chains has been replaced by a tetrathiafulvalene moiety, which can form stable fulvalenium (+ charged form). When one electron is removed, this moiety serves as a storage medium for a "hole," and the molecule becomes a planar field-effect transistor with all of the necessary electrodes located conveniently in one plane.

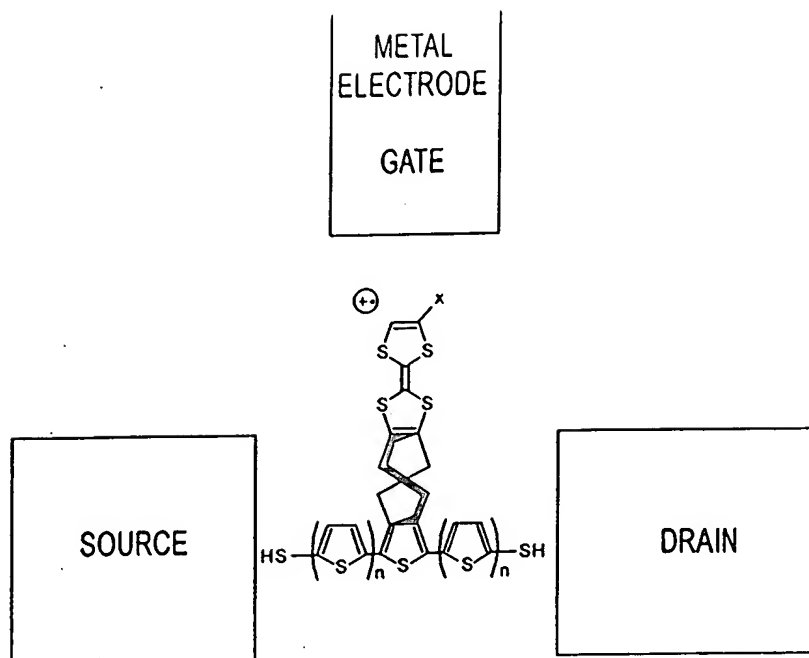


Figure 2 - A planar molecular field-effect transistor.

Table 1 lists several examples of double-well potential molecules, and the experimental data on electron transfer rates in such molecules. The experimental rates range from a few picoseconds to 500 picoseconds, and are representative of the whole class of double-well potential molecules, which numbers in the thousands. Thus, it can be expected that the electron-transfer rate in the proposed transistor, because it is based on double-well properties, will occur within the normal range of electron transfer in this class (1 to 500 picoseconds). Since the electron transfer leads to transistor switching, the important conclusion is that the electron-transfer rate in the double-well potential is also the switching rate of the transistor. A switching rate in the range of picoseconds is a respectable rate that can compare favorably with the known rates of CMOS transistors. A close examination of the table reveals another important conclusion about the electron transfer mechanism: All of the molecules shown are initially neutral, and become charged as a result of the electron transfer. It is apparent that the produced charges are screened by instant polarization of the medium adjacent to the molecules, and thus the electron-transfer rates are not affected. This conclusion is solidified by experimental solvent-dependent rate measurements for the first molecule listed in the table, where the difference of the rates in the polar medium compared to the nonpolar medium was found to be negligible. *It is reiterated that the switching rates are entirely dependent on the electron transfer rates, while the motion of counter ions occurs at a slower pace, and is entirely irrelevant to the switching rate of the molecule.*

Table 2 summarizes the attributes of molecular electronic devices based on double-well potential molecular transistors:

Table 2.

Projected characteristics of molecular field-effect transistor	Parameter
Critical speed of device	10 to 500 ps
Power per transistor without circuit RC	10 pW
On / Off current ratio	1,000,000
Densities	Terabits per sq cm
SRAM memory relative to CMOS	1 molecule vs. 6 CMOS transistors

Table 3 illustrates the differences between the approach taken in this proposal and the other approaches that are under current investigation.

Table 3.

Device	Strength	Weakness
NDR switches	Two terminal devices	Unreliable. Unknown mechanism.
Nanotubes	Reliable transistors comparable to CMOS	Uneven properties from device to device. Not suitable for integration.
Molecular transistors (this proposal)	Three terminal devices. Fast. Lowest power per operation. Highest density. Suitable for integration.	Needs demonstration.

Transistors are very versatile electronic components, since they enable the synthesis of logic and memory. Their availability in molecular form will pave the way to denser memories and cheaper electronic integrated circuits.

#### The basic principles for formation of molecular integrated circuits

*Self-assembly* is a technique that is used extensively in surface science for attaching molecules to surfaces. Certain chemical groups have an affinity for some specific metals and bind spontaneously to them - for example, the specific attachment of SH groups to gold (20) and the attachment of COOH groups to aluminum. Thiol (SH) groups have been used successfully as "alligator clips" in the attachment of molecules of dithiobenzene (a molecule that contains two SH groups) to two gold electrodes simultaneously, with the molecule being used to bridge a gap between the two gold electrodes (21). The same technique can be used for attaching larger molecules, provided that there is a precise match between the length of the molecule and the size of the intermetallic gap. Self-assembly is the main tool for building molecular integrated circuits (MIC) by the use of the *prepared-surface* method (22). Using this concept, the fabrication of MICs can be achieved in two steps:

1. Surfaces designated to support the MICs are patterned with metal conductors that represent the interconnections of the transistors used in the circuits. The metallic interconnects are laid out in the absence of molecules, leaving gaps in the locations where molecular transistors should be located.
2. The molecular transistors are added to the metallized (prepared) surfaces by self-assembly, bridging the open gaps of the metal pattern.

For this scheme to work, the metals and the end groups on the molecular transistors must belong to an affinity pair (SH / gold, for example), and the length of the molecules must be a good match to the size of the gap they must bridge.



Conventional semiconductor devices are built on semiconductor surfaces by stepwise procedures, a type of fabrication that is elaborate and time-consuming. A state-of-the-art dynamic random-access memory requires about 500 individual fabrication steps. In practice, new wafers are started daily and are processed for a whole year before the individual devices are completed. This procedure, in addition to being slow, is very costly. In contrast, fabrication of molecular-electronic devices will require many fewer fabrication steps, because the individual transistors will be fabricated off-line, by chemical procedures, and incorporated into the device by the *prepared surface* method. It is projected that because of this drastic reduction in fabrication steps, molecular electronic components will be far less expensive than their semiconductor counterparts.

### Nanofabrication

Production of molecular ICs requires the fabrication of millions of multi-electrode nanojunctions with inter-electrode distances of a few nanometers. The size of the nanojunction is determined by the size of the molecule that must be embedded in the junction gap. The precise matching is crucial to the success of the fabrication. Thus, there are two opposing demands: The inter-electrode distances (gaps) are limited by the constraints of lithography technology, while the size of the molecules is limited by the resources and time allowed to the chemistry team.

Two lithography technologies are suitable for the formation of molecular ICs: Electron-beam (e-beam) technology and Extreme UV Lithography (EUVL) (23).

E-beam lithography is a sequential method for pattern formation and is therefore extremely slow, but it is very well suited for laboratory exploration. (It is not suitable for commercial applications in which large quantities of ICs must be fabricated.) A projection-lithographic technology, which uses extreme UV light at 13.5 nm, is called EUVL. It can produce resolution of 10 nm (lines in space). It is currently being developed by a consortium of companies comprising manufacturers of semiconductor ICs and equipment manufacturers.

In commercial applications, EUVL is the only promising technology for molecular electronics and for nanotechnology in general. It is based on the fact that resolution in optical lithography is normally expressed by the following formula:

$$R = k_1 * \text{wavelength} / N_A$$

The numerical aperture ( $N_A$ ) is equal to  $\sin(\text{half angle})$  and is limited to 1. The softest parameter is  $k_1$ ; it depends on mask, illumination mode, and resist. Current lithography is printing 130-nm half-pitch lines with 248-nm wavelength and  $N_A = 0.80$ . Therefore,  $k_1 = 0.42$ . Experience has shown that  $k_1$  values have been decreasing over the years and will be further reduced in the future, to values of 0.35 and below.



If 10-nm lines must be printed with 13.5-nm wavelength and  $k_1 = 0.35$ , the  $N_A$  must be 0.4. A recent large-field design for  $N_A = 0.25$  has been reported (24). Designs with larger- $N_A$  are challenging, but can be obtained. Alternatively, one can use so-called Schwartzschild optics, which enable much higher  $N_A$ , but with a maximum field of 1 mm x 1 mm.

From this discussion, it is evident that the right lithography will be available for commercialization of molecular electronic technology, to coincide with the conclusion of this research effort.

### Technical objectives

The following objectives are designed to demonstrate molecular IC technology. The successful implementation of these objectives will bring to market a useful new technology and will effectively resolve the current uncertainties of CMOS scaling.

**1. Synthesize planar field-effect transistors that contain spiro and other bridges.**  
The synthesis of the planar version of the molecular transistors has not been attempted. The proposed research will yield these important materials with dimensions corresponding in size to the dimensions of planned circuitry gaps.

**2. Prepare patterned surfaces for testing of single molecular transistors.**  
The electrical characterization of individual transistors, or logic gates containing them, requires patterned metal electrodes on surfaces. This step entails the preparation of surfaces containing the metallurgy in proper arrangements on the nanoscale. The metals should be chosen to match the self-assembly properties of the alligator clips attached to the molecular transistors, and the gaps should match the length of the molecules. This can be achieved with e-beam lithography applied to thin metal films.

**3. Wire molecular transistors into logic gates and simple circuits such as "half adders."**

The next step in the sequence of circuit formation is the incorporation of transistor molecules in the designated gaps. The attachment is done by self-assembly techniques. In essence, the patterned surfaces are dipped into a solution containing the molecular transistors. Molecules present in the vicinity of the gaps eventually contact the walls of the gap metal and bind to it with the provided alligator clips. Usually the attachment is perpendicular to the surface (or close to it), enabling the molecules to attach themselves to the adjacent electrodes, thus bridging the gaps. This process is analogous to the attachment of substrate molecules to the active sites of enzymes.

**4. Determine the physical properties and electrical characteristics of the simple molecular devices.**

At this point, the circuit is in place and the actual measurements can commence. Measurements should be taken of drain currents vs. gate voltage, drain current vs. drain voltage, threshold voltage, gain, and switching speed.

**5. Design and build an integrated molecular circuit of commercial value.**

To make a smooth transition to commercialization, it would be advantageous to be able to demonstrate a practical circuit that will highlight the attributes of molecular technology. Such attributes are perceived to be a) high circuit density; b) low power density; c) relatively low fabrication cost; and d) high-frequency switching. The actual components that will be demonstrated are SRAMs, DRAMs, and logic circuits. These circuits will not be designed to compete with existing commercial components.

**6. Test prototypes**

Testing of planned devices including high-density DRAMs, SRAMs, and logic will determine the success or failure of the project. These tests are very complicated, and specialized equipment and expertise are required in order to carry them out successfully.

The objectives described above will be fulfilled by specific tasks designed to accomplish the desired results. Some of the tasks flow in sequence, while others can be undertaken in parallel. In the interest of saving time, when possible, projects will be carried out in parallel, on the assumption that critical steps will yield successful results. For example, in the first objective the chemistry could be done in parallel with the preparation of the metallurgy. The tasks are described in the following section..

## **The R&D Plan**

### **Research strategy**

The outlined objectives can be addressed by specific tasks, which are designated as follows:

Task 1 is designed to achieve objective 1. Tasks 2 and 3 are designed to achieve objectives 2 and 5. Task 4 will fulfill objective 3. Task 5 will address objectives 4 and 6.

The synthesis of the molecular transistors should be straightforward, but their incorporation into circuits presents some challenges that have to be addressed by a proper strategy.

As outlined earlier, the *self-assembly* technique will be employed to direct the molecules to the respective locations in the circuit. However, examples exist in the

literature only for connecting molecules to one or two terminals, and the transistor molecule has three terminals. Because of the  $C_{2v}$  symmetry of the molecule, the source and drain terminals are symmetric and interchangeable, while the gate terminal must be connected to a specific gate electrode.

A solution to this challenge can be achieved by a clever design of the interconnect metallurgy. By distinguishing between the gate-electrode metal and the metal used for the source and drain electrodes, an opportunity arises to direct the three terminals of the molecule to the proper arrangement. This can be accomplished by providing the molecule with specific alligator clips for binding the source / drain ends of the molecule to source / drain electrodes, and a specific alligator clip for binding the gate end of the molecule to the gate electrode. For example, the gate electrode can be made of aluminum, which will couple specifically to a phosphate alligator clip on the molecule, (gate chain) and the source / drain electrodes can be made of gold or platinum, which will couple specifically to -SH alligator clips on the corresponding chain. These considerations guide the design of the molecules (task 1) and the design of the metal-electrode patterns (task 2).

Another important consideration is the mixed-valence nature of the molecule; i.e. how do we guarantee that all of the molecules in the circuit have the proper mixed-valence structure? This can be achieved by chemical, photochemical or electrochemical means. The chemical approach relies on equilibrium, and by its nature it cannot provide a complete and uniform distribution of mixed-valence compounds. The photochemical approach is also imperfect, since it can produce doubly oxidized compounds. The only promising approach is the electrochemical. According to this approach, the electrodes that bind the source and drain terminal can be used to perform electrochemistry on the molecules that are bound to their surface. The material of choice for such an operation appears to be platinum which is known to perform excellently in electrochemical processes. Platinum works also well in self-assembly, binding to -SH groups as well as gold.

These considerations suggest the following plan: The circuit will be made of platinum for the source and the drain connections, and of aluminum for the gate connection. The molecules will contain -SH groups on the source and drain terminals and phosphates on the gate terminal. The molecules will be attached to the three terminals by self-assembly, either as neutral species or as doubly charged species. After the attachment, the surface will be immersed in an electrolyte, and a voltage will be applied sequentially to each of the source electrodes. The polarity will depend on the oxidation state of the molecule. If doubly charged, the electrode will have a negative polarity. The molecule will be reduced by one electron only. Cyclovoltametry experiments have shown very well controlled one- or two-electron reductions or oxidations of similar compounds (16) at distinct voltages. *In this way, all of the molecules in the circuit can be prepared in mixed-valence state without corrosion of the electrode metal.*

The interconnecting patterns will be implemented in task 3 by e-beam lithography with PMMA as the e-beam resist. The molecules in the circuit and the electrochemical reduction at the Pt electrodes will be achieved by task 4, while measurement of the transistor properties and the circuit properties will be conducted in task 5.

## The planned work

### Task 1 - Synthesis of molecular transistors

a. It is important to note that the compound must contain an axis of symmetry ( $C_{2v}$ ) and a plane of symmetry. The reason for the first is that in the process of attachment of the transistors in the gap by self-assembly, there should be no ambiguity in the way the molecules settle in the gap: left to right and right to left should be equivalent. In addition, the "gate" chain should have a different alligator clip than the "channel" chain, because it will have to attach itself specifically to the gate electrode, which is fabricated from a different metal than the "source / drain" electrode metal. The synthetic pathway is shown in Figure 3.

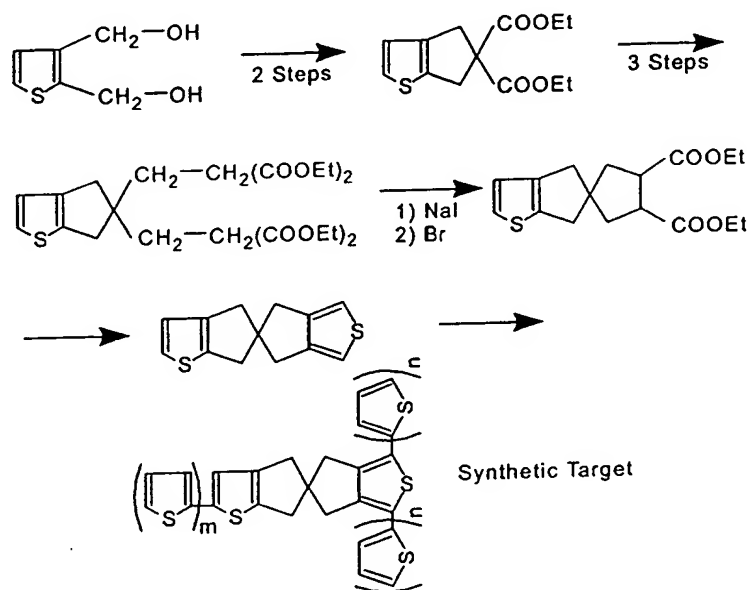


Figure 3 - The synthetic scheme of targeted planar molecular transistors.

To obtain different alligator clips for the gate and for the channel chain, the gate and the channel will have to be connected in two steps.

b. Synthetic variations on the initial chemical structure of the transistor will be performed to optimize the properties of the device with respect to performance.

This task will be carried out in the company laboratory.

## Task 2 – Circuit design for objectives 2 and 5

The circuit design for incorporation of transistors between three electrodes for characterization of the transistor properties without integration is relatively simple. Basically, the three electrodes are separated by gaps. The design is done by CAD computerized techniques.

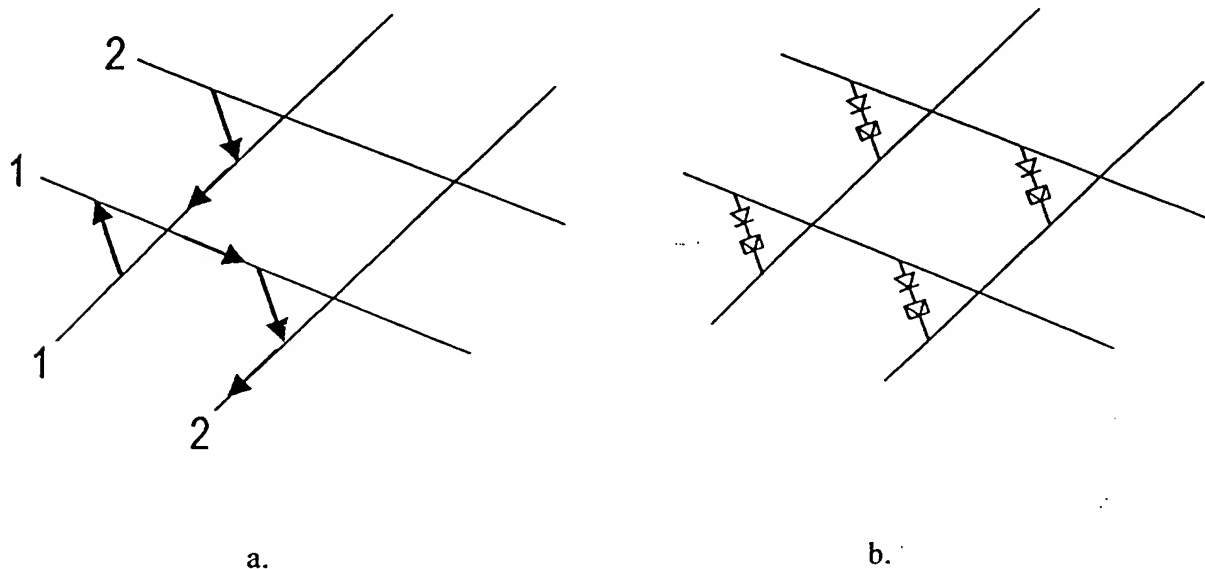


Figure 4 - a. A matrix address memory using latching On / Off switches at intersections, and the false message that can be obtained. b. Solution to the problem indicated in 4a.

A more ambitious task is the design of complete circuits to fulfill objective 5. In this case, a deep understanding of computer architecture is needed. The SRAM project will take advantage of the latching property of the molecular transistor. In a latching transistor, when the channel is switched ON, the device persists in conductive mode until an electric field switches it back to OFF. Such a property can be used for memory in a cross-matrix arrangement. However, this is not simple, as is evident from the example shown in Figure 4a. The figure shows a memory matrix comprising four junctions. If three of the junctions are in the ON state, a scanner probing for the state of the fourth junction will read a false ON signal. The current flow in the matrix provides the illusive signal. This illusive current flow can be arrested by the introduction of a rectifier at each junction, thus permitting the formation of memory matrixes, as shown in Figure 4b. The rectifier can be built into the conductive lines of the circuit.

A proposed SRAM circuit design built from latching molecular transistors is shown in Figure 5. Attempts will be made to design and build small SRAM devices based on this design for demonstration purposes.

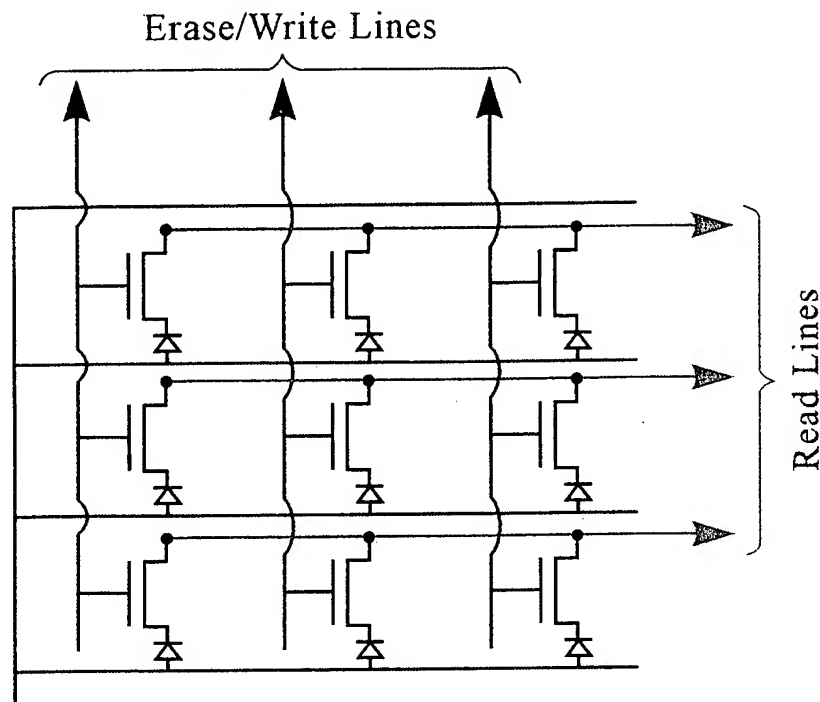


Figure 5 - A proposed SRAM circuit using latching molecular transistors.

The circuit design will also be done by CAD and will be carried out in our laboratory.

### Task 3 – Thin-film patterning

The interconnect wires for the circuit are made by patterning thin metal films by means of lithographic techniques. It is emphasized again that the gate metallurgy should be different from the source / drain metallurgy. Examples are aluminum for the first and platinum for the second. Gaps provided by the lithographic process will match the length of the transistor molecule which will have to bridge those gaps. This task will be carried out at CNF, Cornell University, by e-beam lithography. The center owns a Leica e-beam writer, VB6, which is capable of writing patterns with 4-nm linewidths. The patterns that will be written initially will fill the needs of objective 2. This will be followed by lithography for advanced devices such as SRAMs, DRAMs, and logic, in order to accomplish objective 5, based on the design obtained in task 2.

Nanometer-size metal patterns are fabricated in several steps (for convenience, they can be produced on silicon chips):

Step 1 – Passivation of the surface produces an insulating substrate.  
Step 2 – The surface is covered with two layers of PMMA resist. The bottom layer is a copolymer.  
Step 3 – The resist is exposed by e-beam.  
Step 4 – The pattern is developed.  
Step 5 – A plasma-etching descum process follows.  
Step 6 – The surface is metallized.  
Step 7 – The excess metal and resist are removed by “lift-off.”  
These steps produce half the pattern. Because the PMMA resist has poor contrast, it is necessary to create the gaps where the molecules fit by means of two major processing steps. All of these steps will be carried out by our personnel at CNF.

#### **Task 4 – Self-assembly**

The next step in the assembly of the molecular circuits by the “prepared surface” approach involves the addition of the transistors in their assigned locations. The process for bringing the transistors to their targets is the self-assembly technique. This technique is very simple in concept, as explained previously, but requires appropriate care and equipment in order to prevent contamination. In this case, controlled-atmosphere boxes will be employed to exclude oxygen and moisture. Ideally, the electrical testing of these devices should be carried out in the same box; otherwise, encapsulation of the device should follow.

To accomplish the self-assembly process, the patterned surfaces are dipped into a solution that contains the molecules. This is followed by repeated rinsing steps to remove all of the residual material that has not been chemically bound to the surfaces of the electrodes.

Proper self-assembly is the most critical task of the project, and it carries the most risk. Therefore, much attention will be devoted to it in order to ensure the success of the project. All of the work will be done in our laboratory. Some analytical measurements (such as Auger spectroscopy) will be farmed out as analytical services.

#### **Task 5 - Electrical characterization**

A major objective of the project is the characterization of transistors as individual components and as components of small and large circuits. The task will be assigned to a team of physicists and electrical engineers who will examine the device properties. The measurements are standard tests for transistors in semiconductor technology:

1. Drain current as a function of drain voltage with source at ground and with constant gate voltage. This test is performed at various gate voltages.

2. Drain current as a function of gate voltage (above and below threshold). In semiconductor technology, the drain current of a transistor at subthreshold slope is 60 mV of gate voltage per decade of drain current.
3. Determining the capacitance of the device for the figure of merit of  $CV/I$ . This quantity is a measure of the performance of the transistor because it gives the switching delay of the device.
4. Measurement of the transconductance ( $G_M$ ), the change in drain current for a given change in drain voltage. This parameter gives the maximum oscillation frequency ( $f_{max}$ ) at which the transistor can operate.

While these measurements are simple in principle, in practice they must be performed under inert atmosphere devoid of oxygen, moisture, and other contaminants, which may obscure the device properties. In addition, the low currents expected for individual devices (picoamps to nanoamps) and the high frequencies expected (picoseconds to nanoseconds) require state-of-the-art electronic test equipment which we have already purchased.

B For measurements of complete circuits for DRAM, SRAM, and logic, advantage will be taken of commercial test equipment such as the one offered by MOSAID Systems, and will be performed by a specialized test engineer. The theory of these measurements is given in specialized texts (25).

#### Graphic description of the project plan

Major Project Tasks	Project Time			Major Milestones	Metrics
	Y1	Y2	Y3		
Task 1 Synthesis of transistors Subtask a Subtask b	→		→	Synthesis of the target molecular shown in figure 3. Synthesis of variations on the molecular target for properties optimization. Provision of proper "alligator clips"	Chemical analysis of products and verification of molecular structures. Risk factor - low.
Task 2 Circuit design Subtask a Subtask b	→	→		Design of electrode-test patterns for testing individual transistors. Design of chip architecture and corresponding circuits.	Graphical output of CAD modules. Risk factor - low.
Task 3 Thinfilm patterning			→	Actual implementation of the designs of task 2 by e-beam lithography for metal-patterns formation.	Verification of patterns by electron microscopy and by atomic force microscopy. Verification of correct metal placement by Auger spectroscopy. Risk factor - low.
Task 4 self-assembly			→	Incorporating the molecules in the gaps provided in task 3 by self assembly techniques to create full circuits. Molecules have to be placed correctly so that transistor gates, sources and drains connect to respective electrodes.	The attachment cannot be verified directly by any known spectroscopic technique. However, the correct connection can be inferred by correct device function. It is necessary to demonstrate correct connection of transistor terminals to proceed. Risk factor - high.
Task 5 Electrical characterization Subtask a Subtask b		→	→	Electrical characterization and evaluation of individual transistor properties. Electrical characterization of circuits and evaluation of device operations.	Electronic-circuit metrology will determine quantitatively the properties and merits of the devices. Risk factor - modest.
Funding Totals (\$K)	762	707	694		



## **Company Information, Equipment, and Management Team**

### **The company**

Qutronics Inc. was incorporated in 2001. It is an equal opportunity employer. The company has leased a research facility at 1725 Front Street in Yorktown Heights, NY. The facility comprises a chemistry laboratory suitable for synthetic chemistry work and an electronics laboratory suitable for measurement of electronic devices. These laboratories are complete with furniture fume hoods, laboratory equipment, and instruments. In addition there are designated areas for future expansion that will contain a clean room and a film-deposition and processing laboratory.

Qutronics owns equipment that is specific for this project.

### **Technical employees:**

Qutronics Inc. was founded by Dr. Ari Aviram. He is also the principal investigator for this ATP proposal. At the time of submission, there are no additional technical employees. However, three scientists will to join the company in January of next year:

The CEO position will be filled by Charles V. Freiman, Eng. Sc. D., Columbia University, currently Director of United Engineering Foundation. Previous positions: Director of IBM Tokyo Computer Science Institute, manager IBM Corporate Artificial Intelligence Project, and many more outstanding scientific and managerial positions.

Ron Roy, Ph.D., Material scientist, worked previously in IBM Research Division.

Arnold Halperin, Dipl. Eng., worked previously in IBM.

A search continues for additional qualified scientists in the areas of organic chemistry, surface physics and circuit design.

### **Administrative employees:**

Two part-time administrative employees are employed for bookkeeping and administrative work.

### **Resume of Ari Aviram, principal investigator**

#### **Education**

Ph.D. in chemistry, New York University, 1975.

#### **Industrial experience**

IBM, T.J. Watson Research Center, 1974-2002

## Potential for Broad-Based Economic Benefits

### National Economic Benefits

The semiconductor industry comprises the world's largest corporations, among them IBM, Texas Instruments, Lucent, Intel, Infineon, NEC, Fujitsu, Hitachi, and Samsung. These companies own and maintain the factories and distribution channels for products such as microprocessors and memories of all types. These components are the engines of all computers and are used in all kinds of products from automobiles to washing machines. The market for such components is huge. According to a report released by the Semiconductor Industry Association (SIA) in June 1999 (26), the global semiconductor market grew the preceding year by 31%. Year 2000 sales have reached \$195 billion, and are expected to increase to \$312 billion by the year 2003 (26).

Market growth is driven largely by the increasing pervasiveness of the Internet and wireless-communications products, expanding semiconductor product segments such as digital signal processors, nonvolatile memories, and optoelectronics. The Internet and communications products have become the growth drivers for the industry. They demonstrate a shift from personal computers, which still remain the largest single market for semiconductors.

It is not easy to predict the future, but if the past is prologue, it is likely that a successful new technology such as the one described in this proposal will have a huge impact on the memory and logic components market. Observations of consumer behavior show that individuals desire higher and higher speed and larger and larger memories. Molecular electronics will respond to these basic human needs and therefore will move toward domination of the high-end components market. In other markets, such as science, engineering, and government, where very large computations are needed, molecular chips will play a role. The molecular chips will open new opportunities for computation in areas where computing was not previously attempted. For example, the IBM Corporation is developing a new microchip called Blue Gene, which is a massively parallel computer operating at a petaflop per second. In essence, it will have 50 times the computing power of all the supercomputers in the world today. The company decided to undertake this adventurous project because it believes that increased computational power translates into the ability to validate models used in simulation of biological problems. It also believes that life sciences are demonstrating explosive growth and are creating the most significant industries of this century, hence becoming a huge market for its products. The Blue Gene machine will be needed to solve problems in genomics, bioinformatics, and high-throughput screening of drug candidates. This example strengthens the argument that massive computing machines, which could be the fruits of this proposed research project, will be in high demand in the next decade.

It is fair to expect that the new technology will capture at least 5% of the semiconductor components market within a few years of emergence, and continue to grow market share in subsequent years. Admittedly, the number 5% is arbitrary. It is cited to establish a

realistic limit in order to avoid inflated claims. Assuming that the predictions are for the year 2008, when the semiconductor market may reach \$400 billion per year, a well-managed and well-financed molecular electronics components company will have yearly sales of \$20 billion.

The successful completion of this research will produce results which have an excellent chance of being embraced by the industry for its own benefit and for the ultimate benefit of the end users and the nation. Therefore, there is a high probability that commercialization of this research will be carried out in partnership with current industrial enterprises.

#### **Pathway to economic benefits.**

The initial target product will be a large SRAM memory chip. This can be accomplished by using latching molecular transistors. The advantage offered by such products is that they will encounter little competition. SRAM memory cells that are currently available on the market require six transistors. Consequently, the memory density of SRAMs is a fraction of that of the more popular DRAM, and their prices are also higher. In a typical application the SRAM memory need not be constantly refreshed; therefore, personal computers that utilize SRAMs can be started instantly, with no need to load memory data from hard disks. This is a very attractive commercial feature. There are competing devices in research pipelines that may become commercial in five or six years. These are chips based on magnetic random access memories (MRAMs). Still, MRAMs will be quite expensive components compared to the less expensive molecular SRAMs.

Commercialization of molecular technology will require additional capital. For this purpose, discussions with a large company and with two venture capital companies have begun.

In a different scenario, the first customers or partners will be manufacturers of microelectronic devices, who may be interested to purchase and use this new molecular technology. The semiconductor industry is highly motivated to continually improve its products by bringing to market novel devices containing more and more transistors per chip. Every improvement is embodied in a new generation. When a new generation goes into production, the factory that produced the previous generation is regarded as obsolete. This implies that switching to a new technology of the kind outlined in this proposal will not be different from the common practice of the industry, of switching from one generation of devices to another. However, it is reiterated that a technology based on molecular transistors, which will require substantially fewer fabrication steps, will solve the projected high fabrication costs of conventional electronic components. It will offer much denser memories and logic, as well as a large number of new electronic devices. Faced with all of the difficulties enumerated in the introduction section of this proposal, the semiconductor industry will be motivated to adopt new approaches for electronics devices. If such a scenario prevails, molecular technology will branch out into unprecedented applications.

## Need for ATP funding

The proposed research is largely based on theoretical results which have been implemented in part in a random mode. There has not yet been a demonstration of a complete integrated molecular circuit. We have encountered resistance from the venture capital community with respect to investing in this project. Their contention is that it is too early for them to invest in this project; however, if the project were more advanced, they would be eager to participate. The ATP program can help to move the project over the initial barrier, into a zone where companies and investors will feel secure in making the investments that will be needed for commercialization.

## Risk and reward

The molecular electronics technology described in this proposal is based on a number of published theoretical and experimental results which have been accumulated over the last 12 years. These publications were submitted by reputable scientists who are known for a body of world-class work, as well as for their publications in this field. However, as is customary in modern science, every theory is considered to be a hypothesis until it is proven experimentally. There is always a chance that some obscure principle has been overlooked in the course of the theoretical research, and that an unaccounted-for property may negate the results. However, this has been the case with every technology that has been developed. The successful development of the proposed technology will elevate the electronics industry to new achievements, and the American and world economies to new levels of prosperity, for the benefit of everyone. We seek the opportunity to partner with ATP and be part of the pioneering team.

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International Business Machines Corporation

Thomas J. Watson Research Center  
P.O. Box 218  
Yorktown Heights, New York 10598  
914/945-3000

Department of Commerce  
ATP Program

May 31, 2002

Dear ATP Program Manager,

Dr. Ari Aviram from Qutronics Inc. has outlined to us in broad terms his company's research plan in the area of molecular transistors and circuits, and has requested our future support for joint commercialization of the technology, should the research be successful.

Our department is engaged in molecular technology research and therefore we are interested in all advances in the field. Consequently, in the event that the research that Qutronics Inc. is proposing yields tangible devices, we will be willing to evaluate them and their technological merit. Should Qutronics' devices be of commercial value, we will weigh at that time the possibility to develop jointly commercial products.

Sincerely,

Dr Thomas Theis, Director  
Department of Physical Sciences



UNITED STATES DEPARTMENT OF COMMERCE  
National Institute of Standards and Technology  
Gaithersburg, Maryland 20899

October 17, 2002

Mr. Ari Aviram  
Qutronics, Inc.  
444 Bramblebush Road  
Croton On Hudson, NY 10520

Proposal Reference Number: 2002-00-5678

Title: Molecular Integrated Circuits

Dear Mr. Aviram:

This is to acknowledge receipt of your proposal in response to the Advanced Technology Program (ATP) Announcement FY 2002. Your proposal has been assigned the control reference number noted above.

You will be notified when review of documents submitted for Gate 1 is complete. If that information is determined to have high merit with respect to our selection criterion for scientific and technological merit, ATP will notify you and request the required additional information be submitted for consideration in Gate 2 within two weeks (14 calendar days) from notification. If you are not asked to submit additional information for consideration in Gate 2, you will be provided a debriefing on the information submitted for Gate 1.

The ATP hotline on 1-800-ATP-FUND will be updated regularly to provide current information on this year's competition status.

Thank you for your interest in the ATP.

Sincerely,

Bettijoyce B. Lide  
Competitions Manager  
Advanced Technology Program

10/714,083

Exhibit B

NIST

**QUTRONICS INC.**  
444 BRAMLEBUSH ROAD  
CROTON, NY 10520

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DATE \_\_\_\_\_

Mar 6, 03

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Dr. B. B. B. B.

PATENT-Prior Art Search

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**Exhibit C**



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**Ari Aviram, Ph. D.**

**Short Summary of Education and Experience**

**Education:** Ph.D. in chemistry, New York University, 1975.

**Academic experience:**

Fordham University at Marymount College, Science Department, Tarrytown, NY,  
Adjunct Professor, 1984 – 2004. -- Teaching chemistry and physics

**Industrial experience:**

IBM Corporation, 1974-2002

Qutronics Inc. Since 2003

**Contributions to Molecular Electronics:**

Dr. Ari Aviram worked at IBM, T.J. Watson Research Center, and was the first scientist to propose molecular-electronic devices, as described in US Patent. 3,953,874. Then, in collaboration with Professor Mark A. Ratner, he developed the theory of molecular rectification. He has shown how asymmetric molecules inserted between two metallic electrodes rectify electricity, and has devised a method for computing the I-V characteristics of the molecules. He also has shown that some bistable molecules can serve as memory elements for computer applications. Ari Aviram developed structures and theories of field-effect transistors based on spiro molecules, and has conducted studies that prove the concept. He has also studied and demonstrated electric-field switching of double-well potential molecules. Dr. Aviram has considerable experience in the area of lithography of micro and nano structures. He worked for ten years developing X-ray lithography and e-beam lithography at the IBM Research Division, producing many new resists and methods suitable in nanotechnology applications. In 2003 he founded Qutronics Inc, where he continues to develop molecular-electronic devices for commercial applications.

See also page 4383, paragraph 1, in “The Genesis of Molecular Electronics”, Carroll et. al., Reference no. 23 in Information Disclosure Documents submitted herewith. Dr. Aviram is credited with some of the pioneering work in the field of molecular electronics. This journal article is one of several articles that cite his work in the field.

**Some Relevant references:**

Molecular rectifiers: A. Aviram and M. A. Ratner, *Chemical Physical Letters*, 1974, 29, 277.

Molecular field-effect transistors: A. Aviram, *Journal of the American Chemical Society*, 1988, 110, 5687; A. Farazdel et al., *ibid*, 1990, 112, 4206.

Electric field switching of double-well potential molecules: A. Aviram and P. Roland, *Annals of the New York Academy of Sciences*, 1998, 852, 339.

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